CHARACTERIZATION OF HYDROCARBON POLLUTANT
BURDENS IN PETROCHEMICAL AND
REFINERY PROCESS STREAMS

by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	ii
LIST OF TABLES.....	iv
LIST OF FIGURES.....	v
CHAPTER	
I. PROBLEM AND BACKGROUND.....	1
Statement of Research Objective.....	1
Background for research	1
Scope of Research	7
II. MANUAL FOR CHARACTERIZING PETROLEUM WASTE	
WATER.....	9
Equipment Needed	9
Sample Preparation and Concentration	12
Preliminary Separation into Groups	16
Preliminary Analysis by Chromatography	19
Chromatographic Separation	20
Individual Identification	21
Quantitative Measurement	23
III. DISCUSSION OF METHOD AND RESULTS.....	25
IV. CONCLUSIONS AND RECOMMENDATIONS.....	45
LIST OF REFERENCES.....	47
APPENDICES.....	49

LIST OF TABLES

Table		page
I	Types of Waste Water Samples Analyzed by EPA..	6
II	The Compositions of Test Solution TS-1 and TS-2.....	13
III	The Compositions of Test Solution TS-3 and TS-4.....	14
IV	Test Solution TS-1.....	26
V	Test Solution TS-2.....	27
VI	Test Solution TS-3.....	28
VII	Test Solution TS-4.....	29
VIII	Results of Analysis in Crude Oil Desalting Water.....	34
IX	GC Analysis of the Neutral Compounds Group in the Crude Oil Desalting Water	40
X	GC Analysis of the Aliphatic Hydrocarbon Compounds.....	41

LIST OF FIGURES

Figure		Page
I	Separation of Mixture of Organic Compounds Modified According to the Method of Shriner and Fuson.....	17
II	Interpolation Method Illustration for UV Calculation.....	24
III	TLC Analysis for Crude Oil Desalting Water.....	35
IV	Infrared Spectrum of Phenolic Compounds Group in Crude Oil Desalting Water.....	37
V	Infrared Spectrum of Neutral Compounds Group in Crude Oil Desalting Water.....	38
VI	Plots of Logarithms of Retention Times against Carbon Number for n-Alkanes Homologous Series..	42

CHAPTER I

PROBLEM AND BACKGROUND

Statement of Research Objective

The objective of this thesis is to develop a simple and practical procedure to qualitatively and quantitatively estimate the volatile organics in process waste waters.

Background for Research

There has been an increasing emphasis not only on controlling the total hydrocarbon effluent from plants of the chemical process industry, but also in identifying individual pollutants in process streams. With the recent passage of the Toxic Substances Control Act in the United States, the identity of pollutants in process waters will likely be receiving even more attention.

There are several levels of sophistication which may be used in determining the identity of pollutant compounds in process waters. Perhaps the most detailed analysis for low to moderate molecular weight hydrocarbons comes from the combination of gas chromatography - mass spectrometry (GC/MS). A number of researchers have been active in

using these techniques with a variety of industrial and municipal streams. The GC/MS techniques, while very complete and effective, require very expensive equipment and highly skilled personnel for interpretation of the results.

At the opposite extreme of sophistication are the fairly simple measures of pH, BOD(Biochemical Oxygen Demand), and COD(Chemical Oxygen Demand) which are currently used in waste treatment plant design. These indicators of pollutant burden supply only a nonspecific quantizing of amounts present. However, high levels of organic compounds in industrial effluents, as evidenced by these gross pollution parameter measurements, often do reflect a serious environmental problem.

What is needed is a relatively simple water quality characterizing procedure for concentrating and isolating organic materials from process or waste water so that they can be readily identified.

Various procedures and combinations have been reported in the literature for the determination of organics in water. Jungclaus et al.(1) utilized dichloromethane to concentrate trace organic compounds in two tire manufacturing plant waste waters, followed by preliminary analysis with flame ionization gas chromatography. Final analysis was done on a GC/MS system. The identification of compounds

in the waste water extracts was based on coincidence of gas chromatographic retention times and on equivalence of electron impact and chemical ionization mass spectra with those of known compounds. The problem at one plant was due to large amounts of fatty acids, that at the other site was mostly benzothiazole and 2-mercaptobenzothiazole.

Games et al.(2) analyzed the waste waters from dye manufacturing plant effluents by using a procedure similiar to that of Jungclaus. The majority of the organic compounds found were aromatic amine derivatives. Thiadiazoles and anthraquinone derivatives were also present.

Pitt el al.(3) used low temperature vacuum evaporation as the concentration method for municipal sewage treatment plant effluents and natural waters. They utilized high-resolution liquid chromatography for separation followed by sequential use of ion-exchange chromatography, ultra-violet spectrophotometry, gas chromatography and mass spectrometry for identification of specific compounds. In the primary and secondary effluents from a domestic sewage treatment plant, fifty-six organics and thirteen organics, respectively, were identified and quantified. A total of sixteen different organics have been identified in samples from five different natural waters. Jolley et al.(4) applied a similiar procedure to a domestic

sanitary sewage treatment plant. Thirty-six organics were identified in the primary treatment effluent and nine organics in the secondary treatment effluent. The organic compounds included many different classes; carbohydrates, polyols, glycosides, sulfate conjugates, nucleosides, purine and pyrimidine base, amino acids and carboxylic acids.

Wedgwood et al.(5) used chloroform to extract the organics from chemical industrial effluents and sewages. The hydrocarbons were separated from acids, phenols, bases and oxidized hydrocarbons by passing them through an adsorption chromatographic column. The ultraviolet absorption spectra of successive fractions of the eluate were compared with those of pure compounds. Some polynuclear hydrocarbons were identified from a chemical industrial effluent and the final sewage effluent.

Rosen et al.(6) used activated carbon filters to absorb the organic materials in the waste effluents of five petroleum refineries. The organic residues adsorbed on the surface of the carbon were extracted with chloroform. After extraction, the organic extract was separated into groups by using a modified group separation method of Shriner and Fuson(7). By using adsorption chromatography, the neutral compounds group was further separated into aliphatic, aromatic and oxy-compound fractions. Hydrocarbon

fractions were identified by the resemblance of their infrared spectra to those of refinery waste hydrocarbons.

Creed(8) used liquid chromatography equipped with an ultraviolet detector and a gradient elution system to concentrate and isolate organic materials from water. The isolated component can be followed by individual identification. Several liquid chromatograms of water samples were compared to estimate the existence of some possible organics.

Chakraborty et al.(9) utilized chloroform to extract the hydrocarbons from soot samples. The polycyclic aromatic hydrocarbons were eluted from an adsorption chromatographic column by using benzene as the eluent. A gas chromatograph equipped with a thermal conductivity detector was used for fraction collection. The final individual polycyclic aromatic hydrocarbon identifications were based on their GC retention times and by comparing their specific absorptions in the ultraviolet(UV) region to those of pure compounds. Fifteen polycyclic hydrocarbons were identified by these techniques.

E.P.A.(10) has developed a miniplant extraction facility to study the mass transfer problems between various solvents and water. During the experiments, several prepared aqueous solutions and industrial waste waters were treated

by solvent extraction in a rotary disc contactor. The solvents used were volatile solvents, such as isobutylene and n-butane; less-volatile polar solvents, such as n-butylacetate; and mixtures of volatile and polar solvents, such as isobutylene and n-butylacetate. An important aspect of the experiment approach for actual waste waters involved the identification of the individual pollutants present. Seven separate types of waste water samples were obtained from petroleum and chemical companies and were treated in the above miniplant.

TABLE I

TYPES OF WASTE WATER SAMPLES ANALYZED BY EPA(10)

Lube oil refining.

Cresylic acid recovery.

Ethylene quench.

Oxychlorination.

Phenol-formaldehyde resin manufacture.

Hydrofiner condensate.

Styrene manufacture.

The analytical method for the pollutants identification in each waste water stream was the comparison of the retention times in gas chromatography. This simple analytical procedure can be applied only because the number of expected pollutants in each waste water was not large, and because their identities were semi-qualitatively known. The major organic pollutants in each waste water solution and the aqueous raffinate after extraction were analyzed by gas chromatography. The results of the degree of concentration with the percent removal of the various organics from each waste water by using different organic solvent were reported(10).

As seen from the few examples above, different analysis procedures have different advantages. With the aid of a GC/MS system, many organics can be precisely identified. The UV detector associated with either gas chromatography or liquid chromatography can only analyze the UV absorbing organics. If IR or GC was used without group separation as the identification method, it was not sufficient for positive identification purposes.

Scope of Research

The goal of this research was to develop a procedure which provides both qualitative and quantitative identification of the major volatile organic compounds in process

waste waters. The techniques and instrumentation required have been deliberately chosen so to be within the technical and financial reach of all but the smallest company laboratories. The techniques presented here are not intended for routine process stream monitoring, but for those times when a fairly complete assay of process stream pollutants is called for.

The organic compounds in the water sample were extracted by volatile organic solvents. The concentrates were separated into five distinct characteristic groups by solubility characteristics. Preliminary analysis of each group was done by thin layer chromatography and flame ionization gas chromatography. Fraction separations within each group were done with a gas chromatograph equipped with a thermal conductivity detector. The retention times were used to control sample division into single peaks. The final identification for each component in each group was based on the resemblance of the infrared spectra and the coincidence of retention times in both gas chromatography and thin layer chromatography.

CHAPTER II

MANUAL FOR CHARACTERIZING PETROLEUM WASTE WATERS

Equipment Needed

Chromatographic Methods:

(a) Gas Chromatography

A gas chromatograph equipped with a thermal conductivity detector is needed for sample fractions collection. A Varian Aerograph Model 920 gas chromatograph with single column was used in this project. Helium was employed as the carrier gas. Columns A, B and C, described below, were used.

A gas chromatograph equipped with a flame ionization detector is needed for the analytical gas chromatograph. A Varian Aerograph Hy-FI III Model 1200 gas chromatograph with single column was used in this project. Helium was employed as the carrier gas. Columns A and B, described below, were used.

Column A: Packed with 10% di-n-decylphthalate and 10% UCON 50 HB 2000, supported on 30/60 mesh acid-washed

Chromosorb P. This copper column was 6 feet long and made from 1/4 in. O.D. refrigeration tubing.

Column B: Packed with 5% Bentone 34 and 5% diisodecyl-phthalate supported on 60/80 mesh dimethyl dichlorosilane treated Chromosorb W. This column was 10 feet long and made from 1/4 in. O.D. copper refrigeration tubing.

Column C: Packed with 10% 1, 2, 3- tris(2-cyanoethoxy) propane supported on 60/80 mesh dimethyl dichlorosilane treated Chromosorb W. This column was 6 feet long and made from 1/4 in. O.D. copper refrigeration tubing.

(b) Thin Layer Chromatography

Silica gel 60 precoated plastic TLC plates were used as the common static phase. The sample was applied to the plate as a small spot. The plate was placed in an appropriate chamber containing a developing solvent or solvent mixture, as described in Appendices I-IV. The chromatogram was partially dried and left in a shallow tank over a few iodine crystals until yellow or light brown spots appeared on it. The components in the sample could then be determined by their R_f value. It is measured directly on the chromatogram by taking the ratio of the distances travelled from the start by a given component (distance a) and the solvent

front (distance b): $R_f = a/b$.

Spectrophotometric Methods

(a) Infrared Spectrometry

An infrared spectrophotometer was used for the infrared spectral analysis. A Perkin-Elmer 457 Grating Infrared Spectrophotometer with double beam was used in this project. Liquid samples were examined neat or in solution by pressing them between two polished sodium chloride cells. A liquid film of 0.01 mm or less in pathlength was usually produced. Solid samples were examined as a mull or a KBr pellet as appropriate.

(b) Ultraviolet Absorption Spectrometry

An ultraviolet spectrophotometer was used for the ultraviolet spectra analysis. A Bausch and Lomb Spectronic 505 spectrophotometer with hydrogen lamp source was used in this project. Quartz cells with 1 cm path length were used for the determination of spectra in solution. Many solvents were available for use in the ultraviolet region. Cyclohexane and diethyl ether were used in this project.

Sample Preparation and Concentration

In order to effectively evaluate the analysis method developed in this work, two different mixtures of organic compounds and water were prepared. A mixture of eight selected organic compounds of different characteristics was used to test the range of applicability of the procedure. The organic compounds (phenol, benzoic acid, aniline, m-nitrobenzaldehyde, cyclohexane, 1-butanol, nonane and 2-hexanone) were prepared in two different concentration test solutions, TS-1 and TS-2 as shown in Table II. A second series of mixtures was prepared to simulate a styrene manufacturing waste water(10). These organic compounds (benzene, ethylbenzene and styrene) were also prepared in two different concentration test solutions, TS-3 and TS-4 as shown in Table III.

Diethyl ether was used as the concentrating solvent for test solutions TS-2, TS-3 and TS-4, while chloroform was used as the solvent for test solution TS-1.

Test solution volumes of 1000 ml were extracted three times with 200 ml volumes of volatile organic solvent. Smaller volumes of water solution were extracted with correspondingly less organic solvent. After extraction, the solvent solution was evaporated to a volume of 100 ml.

TABLE II

THE COMPOSITIONS OF TEST SOLUTIONS TS-1 and TS-2

TS-1 (1000 ml)		TS-2 (500 ml)	
Components	Amount prepared (mg)	Components	Amount prepared (mg)
1. Aniline	255.4	1. Aniline	510.9
2. Benzoic acid	250.0	2. Benzoic acid	500.0
3. Phenol	250.0	3. Phenol	500.0
4. m-Nitrobenzaldehyde	250.0	4. m-Nitrobenzaldehyde	500.0
5. 1-Butanol	250.8	5. 1-Butanol	502.1
6. 2-Hexanone	251.5	6. 2-Hexanone	503.0
7. Nonane	321.2	7. Nonane	502.3
8. Cyclohexane	249.2	8. Cyclohexane	498.3

TABLE III

THE COMPOSITIONS OF TEST SOLUTIONS TS-3 and TS-4

TS-3 (1000 ml)		TS-4 (250 ml)	
Components	Amount prepared (mg)	Components	Amount prepared (mg)
1. Benzene	344.6	1. Benzene	1002.1
2. Ethylbenzene	169.9	2. Ethylbenzene	997.1
3. Styrene	19.9	3. Styrene	996.6

Anhydrous sodium sulfate was added to the organic solutions, and the whole was allowed to stand 24 hours. The organic solution was then filtered and the filtrate subjected to group separation using a modification of the method of Shriner and Fuson(7) as shown in Figure I.

Since many liquid samples might be subject to biological or chemical degradation, care should be taken to preserve their integrity. So, the sample should be analyzed as soon as possible after sample preparation. Liquids can usually be safely stored in glass bottles, flasks or capillaries. Most containers and apparatus used in this laboratory for solution manipulations were glass.

For the sampling in the plant, the place of sampling must be representative of the problem, and if more than one sample was to be collected for consecutive analyses, the place of collection should always be the same. Since problems in liquid sampling can be caused by chemical instability, the sample should be carefully protected from light and sealed from atmospheric gases in an inert container. In addition, the sample container should never be filled completely in order to avoid the passage of the contaminants through the stopper.

Preliminary Separation into Groups

According to the modified Shriner and Fuson method(7), a mixture of organic compounds can be separated into five different characteristic groups - neutral compounds, phenolic compounds, acidic compounds, basic compounds and amphoteric compounds (Figure I).

The 100 ml dry organic solution prepared as described above was placed in a separatory funnel and extracted three times with 40 ml volumes of 5% hydrochloric acid containing 20% sodium chloride. The hydrochloric acid - sodium chloride extracts were combined and adjusted to pH = 12 with 5% sodium hydroxide solution. The resulting mixture was then extracted three times with 40 ml volumes of diethyl ether.

The ether layers were combined and dried over anhydrous sodium sulfate. The dried ether solution was filtered to remove the sodium sulfate. The ether was evaporated to approximately 2 ml volume at 35°C - 40°C. The residue was weighed after the diethyl ether was gently evaporated in the hood over 12 hours. This residue contained the basic organic compounds from the original water sample.

The basic water solution (filtrate) contained the amphoteric compounds. It was neutralized to pH = 7 with

FIGURE I: SEPARATION OF MIXTURE OF ORGANIC COMPOUNDS MODIFIED
ACCORDING TO THE METHOD OF SHRINER AND FUSON

5% acetic acid, and extracted three times with 40 ml volumes of diethyl ether. The ether extracts were combined and dried as previously; the ether was evaporated and the residue weighed. This residue was composed of amphoteric compounds.

The organic layer remaining from the above hydrochloric acid extraction was extracted three times with 40 ml volumes of 5% sodium hydroxide containing 20% sodium chloride. If an emulsion layer was formed at this point, it was broken by the addition of a drop of ethyl alcohol or a little more water. The organic layer was dried with anhydrous sodium sulfate, filtered, and evaporated as previously. The carbon dioxide saturated solution was now extracted three times with 40 ml volumes of diethyl ether. After drying and evaporation of the ether as previously described, the residue was weighed. This residue was composed largely of phenolic compounds.

The sodium bicarbonate - sodium chloride solution was now gently heated and stirred to remove any dissolved ethyl-ether. It was then cooled, adjusted to pH = 1 or 2 with 20% hydrochloric acid, and extracted three times with 40 ml volumes of diethyl ether. After drying and evaporation of the ether as previously, the residue was weighed. This residue was composed of strongly acidic compounds.

Preliminary Analysis by Chromatography

Before further separation and identification are attempted, the components in each group can be qualitatively determined by thin layer chromatography (TLC) and gas chromatography (GC). One portion of each solution group is used for this qualitative analysis followed by further separations. Another portion of each solution group is used for the final quantitative measurements.

For the TLC test, the sample can be applied to the plate by using a small capillary tube with diameter 0.3 - 0.4 mm. Then the sample plate can be eluted in a developing chamber by using an appropriate solvent. The optimum developing solvent for TLC can be found by trying different solvents or solvent mixtures with different solvent strengths on the sample plate. Usually this can be done by trial and error. See Appendices I - IV for choices of solvent mixtures. The criterion for choosing the best solvent or solvent mixture for qualitative TLC separation was to pick the solvent giving the most components separated.

A flame ionization detector can be used for preliminary GC analysis. In order to improve the resolution results, either the operating conditions or the chromatographic

column packing materials can be adjusted. The improvement in operating conditions is usually made by changing the column temperature or the carrier gas flow rate. A new characteristic packing material can be made by coating another stationary phase or mixture of stationary phases on a suitable size support. Information for choosing different stationary phases with different retention indices is provided by McReynolds(11). A new stationary phase with different resolution properties can be chosen by the one which has a certain desired difference in the retention indices for the same reference compound.

Chromatographic Separations

After the optimum separation conditions were found for each group, a gas chromatograph equipped with a thermal conductivity detector was used for fraction collection. The same columns and operating conditions which were used in the GC preliminary analysis can now be used for the GC fraction collection column. Because of the relatively low sensitivity of the thermal conductivity detector, highly concentrated samples were used.

A glass tube 0.3 cm O.D. was used as a trap for sample vapors. The condensing agent in which the glass tube was

immersed was a mixture of dry ice and acetone. Each time a sample of twenty microliters was injected into the GC column. The period of collection was guided by the response of the detector. When the elution of a peak is almost complete (as shown by the return of the recorder pen nearly to zero), the tube was disengaged from the exit port. When the collection was through, the component in each glass tube was transferred with a suitable volatile solvent, such as diethyl ether or dichloromethane. After evaporating the solvent from each fraction, the residue was subjected to infrared spectroscopy for qualitative identification.

Individual Identification

Infrared analysis can be successfully combined with the aid of other instrumental techniques such as GC or TLC (12) to identify an individual component. The residues obtained in the group separation or fraction separation above could be liquids or solids, all of which can be analyzed by infrared spectroscopy.

Liquid organic samples could be run either as a neat sample or in solution. Neat samples were prepared by placing one or two small drops of the sample between two highly polished pieces of a sodium-chloride cell. This produces a liquid film pathlength 0.01 mm or less. Then the

infrared spectrum was recorded. Solution samples were obtained by dissolving the liquid sample in an appropriate solvent and placing it in a sodium chloride cell. A variety of other cell materials are available (12), but were not used in this study.

Solid organic samples can be run as solutions, mulls or solid pellets. The solution samples were prepared as before.

For insoluble solid samples, the mull technique usually gave a good qualitative spectrum. The samples were ground to a fine powder using a mortar and pestle, a drop of Nujol (paraffin or mineral oil) was added, the mixture was homogenized to form a paste which was pressed between two salt windows forming a thin, translucent film. The spectrum of the mull was then recorded in the same way as for a neat sample.

The popular KBr pellet technique was most useful for insoluble solids when insufficient sample was available for a mull. The pellets were prepared by carefully grinding a mixture of the sample and potassium bromide until the mixture was composed of very finely ground particles. Usually the sample was 1% dispersed in KBr. The finely ground mixture was then pressed into a transparent

pellet under several tons pressure. The pellet was mounted on a holder, and the spectrum was then recorded.

A general procedure for qualitative interpretation of infrared spectra were found in references 12, 15 and 16. The infrared reference spectra were available in Sadtler Standard Spectra. After the infrared spectra were analyzed, the further identifications for the unknown samples could be made by comparing their retention times to the known compounds by gas chromatography or thin layer chromatography.

Quantitative Measurements

For volatile components, gas chromatography was employed as a quantitative tool by comparison of integrated peak areas of an identified component with standards for that component. In order to improve the results, the integrated peak areas calculated were based on the major solvent peak. Due to possible injection errors, two successive peak areas were not always the same. In order to improve the accuracy in the calculation of concentration, the component peak area in each solution was referenced to the solvent peak area for that solution.

For nonvolatile liquid and soluble solid components, scanning ultraviolet spectrophotometry was the method of

choice. The calculation was based upon the absorption law, known as Beer's Law(16, 17). The interpolation method (Figure II) can be applied to calculate the concentrations of the same solute with an absorbance located on the graph plotted as absorbance vs. concentration. If we assume three different solutions with the same kind solute were prepared as three different concentrations C_1 , C_2 , and C_3 . They give three absorbances A_1 , A_2 , and A_3 in the UV spectra. The concentration of a solution with the same solute could be calculated from the following graphs, if its absorbance was located on the curve made by three solutions.

Figure II: INTERPOLATION METHOD ILLUSTRATION FOR UV
CALCULATION

CHAPTER III

DISCUSSION OF METHOD AND RESULTS

Laboratory Test Solution Results

Four laboratory prepared test solutions were analyzed by the methods described above for organic compounds. For the test solutions TS 1-4, the identifications, along with approximate recoveries of the compounds from the original sample, and the methods for confirming qualitative identifications, are listed in Tables IV through VII.

Test solution TS-1 was prepared as 1000 ml aqueous solution with approximate solute concentration of 250 ppm. The prepared test solution TS-1 was extracted with 200 ml of chloroform, three times, as the initial concentration step. The combined chloroform concentrates were separated into five different characteristic groups by sequential triple extractions using 5% hydrochloric acid - sodium chloride solution 200 ml each, 5% sodium hydroxide - sodium chloride solution 200 ml each, diethyl ether 200 ml each. The detailed solvent extraction procedures were the same as described in the experimental procedure.

TABLE IV

TEST SOLUTION TS-1 (1000 ml)

Component	Amount prepared (mg)	Qualitative Identification		Quantitative Identification	
		By	Amount recovered (mg)	Recovery (%)	By
1. Aniline	255.4	TLC, IR	224.3	87.8	UV
2. Benzoic acid	250.0	TLC, IR	189.7	75.9	UV
3. Phenol	250.0	TLC, IR	208.9	83.6	UV
4. m-Nitrobenzaldehyde	250.0	TLC, IR	140.6	56.2	UV
5. 1-Butanol	250.8	GC, IR	173.6	69.2	GC
6. 2-Hexanone	251.5	GC, IR	236.5	94.0	GC
7. Nonane	321.2	GC, IR	203.6	63.4	GC
8. Cyclohexane	249.2	GC, IR	-----	-----	--

Note: Neutral compounds group includes No.4.- No.8.

TABLE V

TEST SOLUTION TS-2 (500 ml)

Component	Amount prepared (mg)	Qualitative Identification		Quantitative Identification	
		By	Amount recovered (mg)	Recovery (%)	By
1. Aniline	510.9	TLC, IR	364.5	71.3	UV
2. Benzoic acid	500.0	TLC, IR	560.2	112.0	UV
3. Phenol	500.0	TLC, IR	674.7	134.9	UV
4. m-Nitrobenzaldehyde	500.0	TLC, IR	458.6	91.7	UV
5. 1-Butanol	502.1	GC, IR	403.5	80.4	GC
6. 2-Hexanone	503.0	GC, IR	499.8	99.4	GC
7. Nonane	502.3	GC, IR	371.0	73.9	GC
8. Cyclohexane	498.3	GC, IR	476.4	95.6	GC

Note: Neutral compounds group includes No.4 - No.8.

TABLE VI

TEST SOLUTION TS-3 (1000 ml)

Component	Amount prepared (mg)	Qualitative Identification		Quantitative Identification		
		By		Amount recovered (mg)	Recovery (%)	By
1. Benzene	344.6	GC, IR		266.9	77.5	GC
2. Ethylbenzene	169.9	GC, IR		126.6	74.5	GC
3. Styrene	19.9	GC, IR		18.5	93.0	GC

Note: Neutral compounds group includes No.1 - No.3.

TABLE VII

TEST SOLUTION TS-4 (250 ml)

Component	Amount prepared (mg)	Qualitative Identification	Quantitative Identification	
		By	Amount recovered (mg)	Recovery (%)
1. Benzene	1002.1	GC, IR	960.9	95.9
2. Ethylbenzene	997.1	GC, IR	919.0	92.2
3. Styrene	996.6	GC, IR	868.5	87.1

Note: Neutral compounds group includes No.1 - ,No.3.

In the neutral compound residue there were some yellow solids and a liquid phase. Two microliters of the liquid phase were injected into the thermal conductivity GC. Three major peaks were present. The GC fraction collection technique was then used for peak isolation. Columns B and C were used. Since two of the components could not be separated very well when using column B, the fraction containing these two components was separated by column C. Three components finally were identified by GC and IR. The yellow solid component was identified as m-nitrobenzaldehyde by using TLC and IR. The quantitative measurement for each liquid component was done by GC, the solid component was measured by UV.

In the acidic compounds, basic compounds and phenolic compounds groups, benzoic acid, aniline, and phenol were identified. The quantitative analyses were done by UV.

The reason why cyclohexane was not detected in test solution TS-1 was that its boiling point is too close to that of chloroform which was used as concentrating solvent in TS-1 solution. When the solvent was evaporated in solution TS-1, cyclohexane was also evaporated with the chloroform.

For test solution TS-2, the same components as in test

solution TS-1 were prepared as 500 ml aqueous solution with approximate solute concentrations of 1000 ppm. After using 600 ml of diethyl ether in the initial concentration step, the rest of the solvent extraction procedures were the same as for test solution TS-1.

The composition and concentration of test solution TS-3 was similar to the major aromatic organic pollutants in the styrene waste water as estimated by EPA(10). The initial concentration step was to extract with 600 ml of diethyl ether. The rest of the solvent extraction procedures were the same as for test solution TS-1. After each group was separated, all three components were contained in the neutral compounds group, hence fraction collection by GC could be used. The GC column B was used.

For test solution TS-4, the components were the same as for solution TS-3. The three components were prepared as 250 ml aqueous solution with approximate concentration 4000 ppm. In the initial concentration step, 80 ml diethyl ether was used three times. The organic concentrates were subjected to the same experimental procedures as solution TS-3 except the amount of 5% hydrochloric acid - sodium chloride solution used was 60 ml. The analytical results were similar to solution TS-3.

Refinery Crude Oil Desalter Water Analysis

The plant process water used in this analysis was the crude oil desalting water from Cosden Oil and Chemical Company. Volumes of 1000 ml water solution (pH = 5) were used in this analysis. The water was extracted three times with 200 ml of diethyl ether in the initial concentration step. The organic extract solution was filtered using Whatman No.1 qualitative filter paper. The total volume of the ether solution was reduced to 100 ml by evaporating part of the solvent from the solution. This is because small volumes of solution can reduce errors due to experimental handling loss.

The concentrated organic compound solution was separated into five different characteristic groups by sequential triple extractions using 5% hydrochloric acid - sodium chloride solution 40 ml, 5% sodium hydroxide - sodium chloride solution 40 ml, and diethyl ether 40 ml. The detailed solvent extraction procedures were the same as described in the experimental procedure.

The preliminary analysis by flame ionization gas chromatography used two microliter volumes of each group's solution. No distinct peaks were present except for the solvent peak in the chromatograms of the four nonneutral

group solutions. The neutral compounds group showed that more than fifteen components were included. After evaporating the solvent from each group, the residue in each group was weighed (Table VIII) and analyzed by TLC (Figure III).

Acidic, Basic, and Amphoteric Compounds Groups

The quantities for these groups were not sufficient for separation into fractions. Thus they could not be qualitatively identified by IR spectrometry. From the TLC chromatograms (Figure III), at least seven components were present in the acid group, seven in the basic compounds group, and two in the amphoteric compounds group.

Phenolic Compounds Group

The phenolic group solution (400 ml ether solution) was preliminarily checked by flame ionization GC. No major peaks were present except the solvent peak.

After the ether solvent was evaporated, the light brown residue weighed 64.9 mg. When this liquid phase residue was checked by a flame ionization GC, seven peaks were present. The technique of fraction collection by using GC and TLC was attempted. After several twenty microliter injections, the residue collected in each separated glass

TABLE VIII

RESULTS OF ANALYSIS IN CRUDE OIL DESALTING WATER^a

Total organic weight is 112.5 mg (1000 ml sample solution)				
Group	Weight (mg)	Weight percentage (%)	Estimated number of components GC ^b	Identified component TLC ^c
Acidic compounds	2.3	2.0	---	7
Basic compounds	0.3	0.3	---	7
Amphoteric compounds	2.0	1.8	---	2
Phenolic compounds	64.9	57.7	7	2
Neutral compounds	43.0	38.2	15	8
				n-octane

^aSample solution courtesy of Cosden Oil and Chemical Company, Big Spring, Texas.

^bGC analyses are in solvent free case and the operating conditions are :

Injector temperature = 200°C. Helium flow rate = 36 ml/min.

Detector temperature = 240°C. Hydrogen flow rate = 33 ml/min.

Column temperature = 105°C. Air flow rate = 360 ml/min.

^cTLC chromatograms are shown in Figure III.

Note: Static phase is silica gel 60 plastic plate.
Developing solvents used for each group are:

Group	Developing solvent
a. Acidic cpds	28%v Acetonitrile-benzene
b. Basic cpds	40%v Ethyl ether-benzene
c. Amphoteric cpds	40%v Ethyl ether-benzene
d. Neutral cpds	100%v Benzene
e. Phenolic cpds (with phenol ref.)	40%v Ethyl ether-benzene

FIGURE III: TLC ANALYSIS FOR CRUDE OIL DESALTING WATER

tubing trap was still not sufficient for IR identification.

The light brown liquid residue was directly analyzed by TLC and IR. The IR spectrum (Figure IV) indicated phenol was the major component in this group. TLC chromatogram (Figure III) showed two spots, one of them was phenol. If the exact amount of phenol was of interest, UV spectrometry could be applied after the pure phenol was separated from the impurity by using liquid chromatography.

Neutral Compounds Group

The GC preliminary analysis showed that more than fifteen components were included in the liquid phase of the neutral group. Approximately half the volume of this group was solid compounds. Attempts to analyze the solid fraction were unsuccessful.

The total amount of any single component was not sufficient to collect fractions by GC. From the IR spectra (Figure V), strong absorptions at 2960 cm^{-1} , 2920 cm^{-1} , and near 2860 cm^{-1} indicated that methyl and methylene groups were present. The aliphatic hydrocarbon compounds were probably included in this group. Retention time comparisons by GC was therefore employed as the analysis technique for this group.

Figure IV: INFRARED SPECTRUM OF PHENOLIC COMPOUNDS GROUP
IN CRUDE OIL DESALTING WATER

Figure V: INFRARED SPECTRUM OF NEUTRAL COMPOUNDS GROUP
IN CRUDE OIL DESALTING WATER

Fourteen aliphatic hydrocarbon compounds with carbon number from six to twelve were compared with the GC chromatogram peaks in the neutral compounds group. The retention times for neutral compounds group by using column B and column A were recorded in Table IX. Column B was used first, followed by column A for those aliphatic compounds whose retention times were the same or close in the column B. The retention times for fourteen aliphatic hydrocarbon compounds in column B and seven in column A were recorded in Table X. From the GC analysis above, n-octane was probably one of the components in the neutral compounds group.

In order to predict more possible aliphatic hydrocarbon compounds in the neutral compounds group, another approach was tried. It consisted of using the relation between the retention time and the carbon number (20). The logarithm of the retention time of members of a homologous series could be plotted against carbon number. In this neutral group, five n-alkanes were plotted against carbon number in Figure VI. The results showed that, when carbon numbers below twelve were considered, n-octane was definitely present in the neutral compounds group.

The analytical results for the crude oil desalting water were already listed in Table VIII. For the acidic compound, basic compound, and amphoteric compound groups, further

TABLE IX

GC ANALYSIS OF THE NEUTRAL COMPOUNDS GROUP
IN THE CRUDE OIL DESALTING WATER

Column B		Column A	
Peak Number	Retention Time (min.)	Peak Number	Retention Time (min.)
1	3.14	1	2.13
2	4.81	2	3.44
3	6.82	3	3.94
4	8.00	4	5.60
5	10.45	5	7.80
6	11.65	6	8.60
7	14.50	7	9.70
8	15.80	8	11.75
9	19.10	9	17.05
10	21.85	10	26.60
11	25.40	11	37.10
12	27.40	12	44.50
13	30.55	13	51.60
14	32.15	14	58.50
15	37.90	15	74.60
16	51.00	16	94.20

Note: 1) GC operating conditions are the same as for Table VIII.

2) Because of the nature of the GC columns used, individual components may not necessarily be detected in the same order between columns. Thus, for example, component 5 from column A is not necessarily the same compound as component 5 of column B.

TABLE X
GC ANALYSIS OF THE ALIPHATIC HYDROCARBON COMPOUNDS

Column B		Column A	
Compounds Name	Retention Time (min.)	Compounds Name	Retention Time (min.)
2,2-Dimethylbutane	3.32	n-Hexane	2.95
2,3-Dimethylbutane	3.43	Isooctane	4.68
3-Methylbutane	3.50	Cyclohexane	4.84
Cyclopentane	3.52	n-Heptane	4.95
n-Hexane	3.64	n-Octane	8.65
Methylcyclopentane	4.12	n-Nonane	15.80
Cyclohexane	4.58	n-Dodecane	100.00
Isooctane	4.65		
n-Heptane	4.76		
2,3,4-Trimethylpentane	5.87		
2,2,5-Trimethylhexane	6.22		
n-Octane	6.82		
n-Nonane	11.11		
n-Dodecane	62.25		

Note: GC operating conditions are the same as for Table VIII.

Figure VI: PLOTS OF LOGARITHMS OF RETENTION TIMES AGAINST CARBON NUMBER FOR N-ALKANES HOMOLOGOUS SERIES

analysis was limited by the amount in each group. Only the number of components and the weight for each group could be measured. For the phenolic compounds group, the phenol was identified as the major component. For the neutral compounds group, the aliphatic compounds were estimated as part of the components, and n-octane was identified as one aliphatic of the compounds in this group.

Summary of Results

After the procedure developed in this project was applied to the crude oil desalting water sample and several prepared test solutions, the analytical results showed the scope to which the developed procedure can be applied. For more dilute polluted waters, a large quantity of sample solution is required for single component identification. For the more contaminated water samples, the analyses can be applied with samples of about one liter. In an individual process stream the analysis may be easier, because the number of pollutants and their identity may be estimated beforehand. The component identification can be approached by using IR, GC and TLC techniques.

Besides the qualitative analysis, the quantitative estimations were also made. For the prepared test solutions, the recovery for each component was measured by using GC and

UV techniques. High recoveries were found for solution concentrations of 1000 ppm or higher. For the crude oil desalting water, the actual concentration for each component was not attempted, but the weight for each group was measured. The analytical results were recorded in Table VIII.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based on the results of this investigation, the following conclusions were reached:

1. Solvent extraction used in assaying the waste water pollutants in a process stream will be most economical when applied to the more highly contaminated streams, concentrations on the order of one thousand ppm or higher. For complex mixtures different classes of compounds can be separated into separate groups by "Group Separation" which simplifies gas chromatographic analysis.

2. Based on test solution results, the organic recoveries are found to be high for most organic compounds when their concentrations are 1000 ppm or higher.

3. To minimize the cost of recovery of the solvent, volatile solvents which are immiscible with water should be chosen. Since diethyl ether has a very high distribution coefficient with most organic compounds, especially to neutral and acidic organic compounds, and it is quite volatile, it is an attractive solvent.

Recommendations

On the basis of the experimental results, the following recommendations are suggested for further study:

1. The distribution coefficients for more different types of organic compounds in different volatile organic solvents need to be measured or prediction techniques for the distribution coefficients need to be devised.

2. In order to predict more possible compounds in one group by using the plots of retention time and carbon numbers, more homologous series should be compared.

3. Use of stirring with a reflux apparatus in the initial solvent concentration step will probably increase the recovery for each compound.

4. The method can be improved by determining quantitatively the component losses due to evaporation using conventional vapor-liquid calculation procedures.

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Appendices

APPENDIX I

SELECTED BINARY SOLVENTS FOR SEPARATIONS ON ALUMINA AND SILICA^a

Alumina		Silica	
ϵ°	Solvent	ϵ°	Solvent
0.00	100% Pentane	0.00	100% Pentane
0.06	3.5% Benzene-Pentane	0.04	4% Benzene-Pentane
0.12	9.2% Benzene-Pentane	0.08	10% Benzene-Pentane
0.18	20% Benzene-Pentane	0.12	19% Benzene-Pentane
0.24	41% Benzene-Pentane	0.16	32% Benzene-Pentane
0.30	70% Benzene-Pentane	0.20	52% Benzene-Pentane
0.36	21% Ethyl ether-Benzene	0.24	90% Benzene-Pentane
0.42	60% Ethyl ether-Benzene	0.28	6% Ethyl ether-Benzene
0.48	10% Acetonitrile-Benzene	0.32	18% Ethyl ether-Benzene
0.54	28% Acetonitrile-Benzene	0.36	40% Ethyl ether-Benzene
0.60	60% Acetonitrile-Benzene	0.36 ⁺	50% Methanol-Benzene
0.66	12% Isopropanol-Benzene		
0.72	25% Isopropanol-Benzene		
0.78	57% Isopropanol-Benzene		
0.78 ⁺	50% Methanol-Benzene		

Note: ϵ° is eluent strength parameter.

Solvent compositions refer to vol% of indicated solvent pairs.

^aFrom reference 19.

APPENDIX II

SOLVENT STRENGTH OF CHROMATOGRAPHIC INTEREST^a

Solvent	$\epsilon^\circ (\text{Al}_2\text{O}_3)$	Solvent	$\epsilon^\circ (\text{Al}_2\text{O}_3)$
Fluoroalkanes	-0.25	Chloroform	0.40
n-Pentane	0.00	Methylene chloride	0.42
Isooctane	0.01	Methyl-i-butylketone	0.43
Petroleum ether,		Tetrahydrofurane	0.45
Skellysolve B, etc.	0.01	Ethylene dichloride	0.49
n-Decane	0.04	Methylethylketone	0.51
Cyclohexane	0.04	1-Nitropropane	0.53
Cyclopentane	0.05	Acetone	0.56
Diisobutylene	0.06	Dioxane	0.56
1-Pentene	0.08	Ethyl acetate	0.58
Carbon disulfide	0.15	Methyl acetate	0.60
Carbon tetrachloride	0.18	Amyl alcohol	0.61
Amyl chloride	0.26	Dimethyl sulfoxide	0.62
Xylene	0.26	Aniline	0.62
i-Propyl ether	0.28	Diethyl amine	0.63
i-Propyl chloride	0.29	Nitromethane	0.64
Toluene	0.29	Acetonitrile	0.65
n-Propyl chloride	0.30	Pyridine	0.71
Chlorobenzene	0.30	Butyl cellusolve	0.74
Benzene	0.32	i-Propanol, n-Propanol	0.82
Ethyl bromide	0.37	Ethanol	0.88
Ethyl ether	0.38	Methanol	0.95
Ethyl sulfide	0.38	Ethylene glycol	1.11
Chloroform	0.40	Acetic acid	large

Note: ϵ° is solvent strength parameter.

^aFrom reference 20.

APPENDIX III
ELUOTROPIC SERIES FOR LIQUID SOLID CHROMATOGRAPHIC ON SILICA^a

ϵ°	I	II	III
0.00	Pentane	Pentane	Pentane
0.05	4.2%v PrCl ^b /pentane	3%v CH ₂ Cl ₂ /pentane	4%v Benzene/pentane
0.10	10%v PrCl/pentane	7%v CH ₂ Cl ₂ /pentane	11%v Benzene/pentane
0.15	21%v PrCl/pentane	14%v CH ₂ Cl ₂ /pentane	26%v Benzene/pentane
0.20	4%v Ether/pentane	26%v CH ₂ Cl ₂ /pentane	4%v EtOAc ^c /pentane
0.25	11%v Ether/pentane	50%v CH ₂ Cl ₂ /pentane	11%v EtOAc/pentane
0.30	23%v Ether/pentane	82%v CH ₂ Cl ₂ /pentane	23%v EtOAc/pentane
0.35	56%v Ether/pentane	3%v Acetonitrile/benzene	56%v EtOAc/pentane
0.40	2%v Methanol/ether	11%v Acetonitrile/benzene	
0.45	4%v Methanol/ether	31%v Acetonitrile/benzene	
0.50	8%v Methanol/ether	Acetonitrile	
0.55	20%v Methanol/ether		
0.60	50%v Methanol/ether		

Note: ϵ° is solvent strength parameter.

^aFrom reference 21.

^bIsopropyl chloride.

^cEthyl acetate.

APPENDIX IV

ELUOTROPIC SERIES FOR LIQUID SOLID CHROMATOGRAPHIC ON SILICA^a

ϵ°	I	II	III
0.00	Pentane	Pentane	Pentane
0.05	8%v PrCl ^b /pentane	1.5%v CH ₂ Cl ₂ /pentane	4%v Ether/pentane
0.10	19%v PrCl/pentane	4%v CH ₂ Cl ₂ /pentane	9%v Ether/pentane
0.15	34%v PrCl/pentane	8%v CH ₂ Cl ₂ /pentane	15%v Ether/pentane
0.20	52%v PrCl/pentane	13%v CH ₂ Cl ₂ /pentane	25%v Ether/pentane
0.25	5%v MeOAc ^c /pentane	22%v CH ₂ Cl ₂ /pentane	38%v Ether/pentane
0.30	8%v MeOAc/pentane	34%v CH ₂ Cl ₂ /pentane	55%v Ether/pentane
0.35	13%v MeOAc/pentane	54%v CH ₂ Cl ₂ /pentane	81%v Ether/pentane
0.40	19%v MeOAc/pentane	84%v CH ₂ Cl ₂ /pentane	4%v Pyridine/pentane
0.45	29%v MeOAc/pentane	1%v MeCN ^f /ether	8%v Pyridine/pentane
0.50	44%v MeOAc/pentane	5%v MeCN/ether	13%v Pyridine/pentane
0.55	65%v MeOAc/pentane	14%v MeCN/ether	20%v Pyridine/pentane
0.60	5%v ProH ^d /ether	36%v MeCN/ether	32%v Pyridine/pentane
0.65	10%v ProH/ether	MeCN	
0.70	20%v ProH/ether		
0.75	3%v MeOH ^e /ether		
0.80	7%v MeOH/ether		
0.85	17%v MeOH/ether		
0.90	40%v MeOH/ether		

Note: ϵ° is solvent strength parameter.

^aFrom reference 21.

^bIsopropyl chloride.

^cMethyl acetate.

^dIsopropanol.

^eMethanol.

^fAcetonitrile.